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Priority: None

Title of the Invention:

Ink Jet Recording Medium

Claims

1. An ink jet recording medium comprising an ink recording layer in a support,

CHARACTERIZED IN THAT

said ink recording layer is consisted of a resin composite containing hydrophilic resin having thermoplasticity, said ink recording layer being formed in a melt extrusion coating method.

2. An ink jet recording medium as defined in claim 1, CHARACTERIZED IN THAT said hydrophilic resin having thermoplasticity has a melting point below 210°C, and a melt flow ratio of 1 - 50g/10 min (at a temperature of 190°C under a load of 2160g).

3. An ink jet recording medium as defined in

claim 1 or 3, CHARACTERIZED IN THAT said hydrophilic resin having thermoplasticity is a copolymer resin containing at least an ethylene unit and a vinyl alcohol unit.

4. An ink jet recording medium as defined in claim 1 or 2, CHARACTERIZED IN THAT said hydrophilic resin having thermoplasticity is a copolymer resin containing at least an acetovinyl unit, a vinyl alcohol unit and an ethylene unit having a hydrophilic radical in the side chain.

5. An ink jet recording medium as defined in claim 1 or 2; CHARACTERIZED IN THAT said hydrophilic resin having thermoplasticity is a copolymer resin containing at least an oxyalkylene radical.

6. An ink jet recording medium as defined in claim 1 or 2, CHARACTERIZED IN THAT said hydrophilic resin having thermoplasticity is a copolymer resin containing at least an ethylene oxide unit.

7. An ink jet recording medium as defined in claim 1, 2, 3, 4, 5 or 6, CHARACTERIZED IN THAT said support is a sheet-like support having a paper backing coated with a resin composite containing polyolefin resin.

## Detailed Description of the Invention

[ 0001]

### Art Field the Invention Pertains to

The present invention relates to an ink jet recording medium, in particular an ink jet recording medium having glossiness and image sharpness equivalent to those of silver halide photographs.

[ 0002]

### Prior Art

Since an ink jet recording method, unlike a heat transfer recording method, does neither require an ink sheet to facilitate maintenance, nor processes for development and fixation as have been required in an electrophotographic method, it is featured by the capabilities to make equipment compact and achieve color recording with higher resolution at a higher speed. Accordingly, an ink jet recording method has been rapidly popularized in recent years as an output printer for personal computers and an output method for a facsimile, or a copying machine. Moreover, with highly improved performance of personal computers and popularization of multimedia, opportunities are increasing for printing out not only documents but color images. There is, thus, an increasing demand for an ink jet recording medium by means of which recorded images can be obtained which are superior in ink absorbing quality and have as high glossiness and image sharpness as silver halide photographs

[ 0003]

Conventionally, for an ink jet recording medium, an ink jet recording medium of so-called plane paper type made up of pulp paper treated with conversion has been generally used. For recording color images, from the viewpoint of the ink receptivities, such as shapes and sharpness of dots, ink absorbing capacity and speed, and

fixation of ink dyestuffs, there has been preferred an ink jet recording medium of coated paper made up of pulp paper coated with an absorbent inorganic pigment, such as silica, and another pigment prepared by mixing adhesives, such as polyvinyl alcohol, polyvinyl pyrrolidon, or gelatin. However, in an ordinary ink jet recording medium of coated paper type, in the process of coating an ink recording layer on the pulp paper and drying it, there may occur uneven shrinkage caused by machine formation of the pulp paper to make the surface more or less rough. It has, thus, been a problem that when there is deficiency in glossiness, or the mixing ratio of an absorbent pigment is increased, the roughness is caused by the particles of the pigment to lower the glossiness.

[ 0004 ]

Japanese patent publication No. 25352/1991 discloses an ink jet recording paper having high glossiness characterized in that on a cast-coated paper having the surface glossiness above 80%, or a support, such as a plastic sheet having Hunter whiteness above 80% there is formed a film containing a bridging agent having vinyl alcohol having a saponifiability of 50 - 90 mol % and vinyl-resistant alcohol of 5 - 50 weight percent. However, even if a cast-coated paper was used as a pulp paper, because it absorbed water once in the process of coating and drying the coating, roughness could not be inhibited from occurring in the drying process, resulting in insufficient gloss. On the other hand, when a plastic sheet was used, roughness attributable to formation of a support was eliminated and high glossiness could be obtained, while a plastic sheet was not only generally higher in cost than a pulp paper but also insufficient in respect of handle, aesthetic property and stiffness, which could not meet the requirements in the market.

[ 0005]

Japanese patent publication No. 212952/1993 discloses an ink jet recording medium having a support provided with an ink receptive layer containing an adhesive, which medium is characterized in that the ink receptive layer contains a hydrophilic adhesive and polyethylene oxide, the polyethylene oxide being present as polyethylene oxide emulsified by cationic activities in the water-based coating material to be used for the ink receptive layer. Also, it discloses an ink jet recording medium having a support made up of a base paper covered with polyolefin or a plastic film. However, when such a base paper covered with polyolefin is used, an ink jet recording medium having high glossiness can be obtained, while in order to achieve ink absorbing quality required for color recording, an ink recording layer must be as comparatively thick as about more than  $15\text{g/m}^2$  in terms of the coating quantity. Normally, an ink recording layer is coated with water-based coating material, while in order to obtain a sufficient coating quantity, the concentration of the coating must be increased, or the quantity of the wet coating must be increased. However, the concentrations of those coatings should be limited usually to about 10 - 20 weight percent. When the concentration was excessively increased, the viscosity of the coating violently increased to make it difficult to be handled in a coater. Alternatively, when the quantity of the wet coating was tried to be increased, not only the coated surface became rough but also, even if coating could be carried out, the drying load of a coater became excessive to cause thermal shrinkage of a base material, resulting in a trouble such as inferior gloss occurring, or lowered productivity.

[ 0006]

#### Problems To Be Solved by the Invention

The present invention solves the above-described problems to provide an ink jet recording medium being superior in absorbing quality and having as high glossiness and image sharpness as silver halide photographs, when applied to an ink jet printer.

[ 0007]

Means to Solve the Problems

The present invention includes the following aspects:

[ 1 ] An ink jet recording medium comprising an ink recording layer in a support characterized in that the ink recording layer is consisted of a resin composite containing hydrophilic resin having thermoplasticity, the ink recording layer being formed in a melt extrusion coating method.

[ 0008]

[ 2 ] An ink jet recording medium as defined in [ 1 ] characterized in that the hydrophilic resin having thermoplasticity has a melting point of below 210°C and a melt flow ratio of 1 - 50g/10 min (at a temperature of 190°C under a load of 2160g).

[ 0009]

[ 3 ] An ink jet recording medium as defined in [ 1 ] or [ 2 ] characterized in that the hydrophilic resin having thermoplasticity is a copolymer resin containing at least an ethylene unit and a vinyl alcohol unit.

[ 0010]

[ 4 ] An ink jet recording medium as defined in [ 1 ] or [ 2 ] characterized in that the hydrophilic resin having thermoplasticity is a copolymer resin containing at least an acetovinyl unit, a vinyl alcohol unit and an ethylene unit having a hydrophilic radical in the side chain.

[ 0011]

[ 5 ] An ink jet recording medium as defined in [ 1 ] or [ 2 ] characterized in that the hydrophilic resin having thermoplasticity is a copolymer resin containing at least an oxyalkylene radical.

[ 0012]

[ 6 ] An ink jet recording medium as defined in [ 1 ] or [ 2 ] characterized in that the hydrophilic resin having thermoplasticity is a copolymer resin containing at least an ethylene oxide unit.

[ 0013]

[ 7 ] An ink jet recording medium as defined in [ 1 ], [ 2 ], [ 3 ], [ 4 ], [ 5 ] or [ 6 ] characterized in that the support is a sheet-like support having a paper backing coated with a resin composite containing polyolefin resin.

[ 0014]

#### Embodiments of the Invention

An ink jet recording medium in accordance with the present invention is obtained by coating with a melt consisted of a resin composition having thermoplasticity, for example, the surface of a support by means of an extrusion coating method, and by cooling and solidifying the coated melt resin composite layer while pressing it against the circumferential face of a rotating cooling roll.

[ 0015]

Conventionally, in the ink recording layer of an ink jet recording medium, hydrophilic resin, such as polyvinyl alcohol prepared as a water-based coating independently, or by mixing with an asorbent inorganic pigment can be used in water-based coating, but not be used in a melt extrusion method, because conventional hydrophilic resin has thermoplasticity at a melting point of about 230°C, while it is easy to be thermally degraded

and there has been nothing to show appropriate fluidity in an extruder, which has caused difficulties in melt extrusion coating. However, in the present invention, hydrophilic resin having thermoplasticity non-degradable even at a melting point of about 200°C is employed to carry out melting and forming in an extruder in a manner similar to that in the case of polyethylene to provide an ink recording layer, thereby obtaining high glossiness and image sharpness.

[ 0016]

Said resin composition consisted mainly of hydrophilic resin having thermoplasticity is subject to melt processing at 150-300°C, preferably in a range of 180-220°C. When the temperature is below 180°, the sheet-like melt becomes poor in fluidity and spreadability in a melt extruder and weak in adhesivity to the supporting body as well, making it inappropriate for processing. Also, when the temperature is above 220°C, there is a fear of decomposition of resin as the case may be. The melting point (JISK 7121) of the hydrophilic resin having thermoplasticity and used in the present invention is not defined in particular as long as melt extrusion coating can take place, while preferably it is below 210°C. A melt flow rate (MFR, JISK 7210) for the hydrophilic resin having thermoplasticity in accordance with the present invention is 1 - 50g/10 min at a temperature of 190°C under a load of 2160g, preferably in a range of 2 - 20g/10 min. If MFR is smaller, there may occur trouble in the melt extruder, such as an excessive torque, or thermal deterioration of the resin. When it is larger, there may occur an unstable quantity of the resin extruded, which in turn causes hindrance to stable operation. The density of the hydrophilic resin having thermoplasticity is not defined in particular, while the density is about 0.7 - 1.5g/cm<sup>3</sup>.



[ 0017]

The hydrophilic resin having thermoplasticity in accordance with the present invention is suitable for use in melt extrusion coating, and as far as it is hydrophilic resin absorptive of ink for an ink jet recording, one or more sorts thereof can be selected for use. For example, copolymer resin containing an ethylene unit and a vinyl alcohol unit can be used. An ethylene vinyl alcohol copolymer (EVOH) or an ethylene acetylvinyl alcohol acetal copolymer resin is preferable. Molar percentage for the respective units of those copolymer resins are not defined particularly. With regard to molar percentage for an ethylene unit, it will do when thermoplasticity is displayed at a melt extrusion temperature, or ink absorbency is displayed as an ink recording layer, while it is desirable to be 25 - 90 mol%. A copolymer resin containing at least an acetyl vinyl unit, a vinyl alcohol unit and an ethylene radical having a hydrophilic radical in its side chain may be used as well. For example, it is a copolymer expressed by the following formula, i.e., expressed as 
$$= (CH_2-CHOH)_l - [CH_2-CH(CH_3-OCO)]_m - (CH_2-CHR1)_n$$
 [where, R<sup>1</sup> is a hydrogen atom or an alkyl radical or a hydrophilic radical (for example, hydrophilic radicals, such as an alkylcarboxyl radical, an acetoacetyl radical, an amino radical and a sulfon radical, or alkyl radicals substituted for by those hydrophilic radicals), and l, m and n are integral numbers equal to or larger than unity].

[ 0018]

Further, polymer resin containing at least an oxyalkylene radical can also be used. For example, it is a polymer consisted of vinyl alcohol containing an oxyalkylene radical as shown by the following formula, i.e., a saponified substance of a copolymer consisted of

acetyl vinyl and an ethylene unsaturated monomer containing an oxyalkylene radical expressed as  $(\text{CHR}^2 - \text{CHR}^1 - \text{O})_p - \text{H}$  [where,  $\text{R}^2$ ,  $\text{R}^1$  are alkyl radicals (in particular methyl radicals or ethyl radicals), and  $p$  is a integral number] is useful.

[ 0019]

With regard to specific examples of an ethylene unsaturated monomer containing an oxyalkylene radical, cited are polyoxyethylene (meta) acrylate, polyoxypropylene (meta) acrylate, polyoxyethylene (meta) acrylamide, polyoxypropylene (meta) acrylamide, polyoxyethylene (1-(meta) acrylamide-1, 1-dimethylepripyl) ester, polyoxyethylene (meta) allylether, polyoxypropylene (meta) allylether, polyoxyethylene vinylether, polyoxypropylene vinylether. The  $p$  representative of the addition molar number of the oxyalkylene unit is about 2 - 300 in either case, in particular, it is desirable that  $p$  is about 5 - 200. Among the above-mentioned, polyoxyethylene allylether, polyoxypropylene allylether, polyoxyethylene metaallyl-ether, polyoxypropylene metaallylether and the like have good thermoplasticity and ink absorbing quality and are of great utility. Polymer resin containing at least ethylene oxide may be used as well.

[ 0020]

They are selectable for use from those on the market, for example by Kuraray Co., Ltd., under the trademark "EVAR" (phonetic) (ethylene vinylalcohol copolymer resin), by Unitika Chemicals under the trademark "UNITIKA RANGE UMR" (phonetic) (saponified substance of ethylene acetylvinyl copolymer), or by Nippon Gohsei Kagaku Kogyo, Co., Ltd., under the trademark "SOANOL" (phonetic) (ethylene vinylalcohol copolymer resin). Further, one made by Kuraray Co., Ltd., under the trademark "KURARAY POBAR CP Series" (phonetic) (methylated vinylalcohol), or one made

by Nippon Gohsei Kagaku Kogyo, Co., Ltd., under the trademark "ECOMATY" (phonetic) (methylated polyvinylalcohol) has thermo-plasticity appropriate for melt extrusion coating and hydrophilic performance appropriate for ink absorption, and thus, it can be desirably used. In addition, one made by Sumitomo Precision Chemicals, Inc., under the trademark "AQUACOCKE" (phonetic) (ethylene oxide polymer), or one made by Daiichi Kogyo Seiyaku Co., Ltd., under the trademark "PAOGEN" (phonetic) (ethylene oxide polymer) may be used as well.

[ 0021 ]

A resin composition composed of hydrophilic resin having plasticity in accordance with the present invention may be mixed with multi-purpose resin, natural high polymer material and pigment properly as required. The quantity of the multi-purpose resin or natural high polymer material is preferably 0.1 - 10 weight percent to hydrophilic resin of 100 weight percent having thermoplasticity. Such mixing enables to provide a resin composition with improved melt fluidity and thus effective in improvement of workability in melt extrusion processing. In addition, the quantity of the pigment is preferably 1 - 100 weight percent to hydrophilic resin of 100 weight percent having thermoplasticity.

[ 0022 ]

On the other hand, as additives, a single or more sorts, out of dyes, such as fluorescent dyes, coloring pigments, antioxidants, ultraviolet absorbents, antistatic agents, bridging agents, antihydrolyzing agents, and cationic resin, can be selected and added in a small quantity. As for multi-purpose resin possible to be mixed, polyethylene, polypropylene, polymethylpentene, polybutene, crystalline polybutadiene, polybutadiene, polystyrene, styrene-butadiene resin, polyvinyl chloride, polyvinyl

acetate, polymethyl metacrylate, polyvinylidene chloride resin, polytetrafluoroethylene, ethylene-polytetraethylene copolymer, ethylene-vinyl-acetate, AS resin, ABS resin, ionomer, AAS resin, ACS resin, polyacetal resin, polyamide resin, polycarbonate resin, polypheniline oxide, polyethylene terephthalate, polybutylene terephthalate, polyallylate, polysulfon, polyether sulfon, polyimide, polyamidoimido, polyphenilene sulfoimido, acetyl cellurose, acetobutyric cellurose, celluloid, cellophane, nylon and the like are exemplified.

[ 0023]

As for natural high polymer materials, starch-based high polymer, cellulose-based high polymer, other polyose-based high polymer, protein-based high polymer and the like are cited as examples. Corn starch, potato starch, sugar cane starch, rice starch, bean starch, physically modified starch, oxygenically modified starch, chemically modified starch, chemically decomposed and modified starch, esterified starch, bridged starch and the like are cited as examples. With regard to cellulose-based high polymer, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl-methyl cellulose, hydroxypropyl-methyl cellulose, hydroxybutyl-methyl cellulose, carboxymethyl cellulose, acetyl cellulose and the like are exemplified. In regard to other polyose-based high polymer, glycogen, xylan, chitin, chitosan, alginic acid, sodium alginate, guar gum, gum, gloiopeltis glue, agar and the like are cited as examples. For protein-based high polymer, collagens, such as gelatin and glue, casein, zein, gluten, blood albumin, soybean protein, pullulan and the like are exemplified.

[ 0024]

With regard to the pigment, amorphous silica,

synthetic silica by a vapor-phase method, synthetic fine grain alumina silicate, kaolin, clay, baked clay, magnesium sulfide, aluminum oxide, aluminum hydroxide, calcium carbide, satin white, crocodile silica, anionic crocodile silica, cationic crocodile silica, alumina-sol, psuedo-boehmite alumina sol, aluminum silicate, smectites, zeolite, diatom earth, montmorillonite group ores, hydrotalcite group ores, smectite group ores, bentonite-group ores, plastic pigments, cereal starch powder particles and the like can be properly selected for use independently, or in mixture. An ink recording layer consisted of the resin composition formed on a support is not defined in particular, while it is coated in a coating quantity of 10 - 100g/m<sup>2</sup> by melt extrusion. However, it has been a problem that in the case of less coating quantity, the film forming stability of the molten resin composite and its adhesivity to the support may get worse, and by contrast, in the case of a thick-coated layer, the ink absorbing quality can be improved, while increasing the quantity cannot expect effects beyond that as well as causes to make the recording material thick, or causes to increase the cost more than need be, rendering it impractical. In view of the balance of the ink absorbing quality, it is preferable to be 20 - 60g/m<sup>2</sup>.

\_[ 0025]

Further, for the purpose of strengthening adhesion of the resin composition to the sheet-like support, anchoring by coating a chemical agent and surface activation processing, such as corona discharging, flaming, low temperature plasma processing, may also be applied on the surface of the support. Also, after gas containing ozone is blown to the face on the side brought in contact with said resin melt discharged from a melt extruder, coating may be applied on the support as required. As a

support, a sheet-like support, such as woodfree paper, coated paper, synthetic paper, a high polymer film or a resin coated paper, may be used, and for further improvement in adhesivity of an ink recording layer, primer processing may be applied as well.

[ 0026]

In the mode of using resin coated paper, as a support, having the surface (or the surface and the rear face) of the paper base coated with a resin composition containing polyolefin resin, both the glossiness and image sharpness can be obtained to higher degrees. Also, the adhesivity of a resin composition containing hydrophilic resin having thermoplasticity to the support is good. For polyolefin resin used for coating either face, or both faces of a sheet-like base, selection can be made from among independent polymers, such as ethylene,  $\alpha$ -olefins, for example, propylene, copolymers consisted of two or more sorts of the olefins and two or more compositions of respective sorts of those polymers. Particularly desirable olefin resins are low density polyethylene, high density polyethylene, directly chained low density polyethylene and a mixture thereof. The molecular weight of those olefin resins are not limited in particular, while usually those in a weight range of 20,000 - 200,000 are used. The coating quantity for each coated layer on the front and rear faces is 10 - 40g/m<sup>2</sup>, which is formed on a sheet-like base.

[ 0027]

A resin composition used for the coated layer may be added with various kinds of additives, such as white pigment, blue pigment, fluorescent whitening agent, antioxidant, fluorescent dyes, lubricant, for the purpose of improving the performance, such as whiteness, color and hiding power that are required. Also, it is allowed to

provide the rear face with a polyolefin resin coated layer by mating. Further, for the purpose of providing antistatic property, printing and writing properties and the like, the surface of the coated layer on the side of the rear face may also be provided with a pack coated layer. Coating of polyolefin resin can be carried out by a melt extruder.

[ 0028]

For a melt extrusion apparatus in accordance with the present invention used in the process of coating a resin composition on a paper base and the process of coating an ink recording layer on a support, a melt extruder (an, extrusion coating apparatus) which is in general so called as a laminator may be used. A laminator flows down a thermoplastic resin composition in the form of film (for example, an ink receiving layer) through an extruder, a T die, to coat the support therewith and then operates pressurized adhesion and cooling between a metallic cooling roll having the support closely adhered and a pressure roll provided with rubber lining. Instead, a cooling roll provided with stripping quality may be used as well. The thermoplastic resin composition is supplied from a hopper of the extruder through a cylinder, melted to be homogenized, and reaches the T die through a screen and a breaker plate to then flow down widely. The melted resin spreads to right and left from the center of the T die and forms a thin film of melted resin. The melted resin film is passed from a feeding section, fallen on a sheet-like base provided with surface treatment on the way as required, whereupon it is adhered thereon and cooled simultaneously by the cooling roll and the pressure roll, and is taken up by a take-up machine. The thickness of the coating layer is adjusted by the discharging quantity and the receiving speed of resin and by a lip of the T die. An

ink jet recording sheet in accordance with the present invention can use a coextrusion laminating method so as to coat a paper base with a polyolefin resin coated layer and an ink recording layer simultaneously as well.

[ 0029]

A separate ink recording layer (a layer containing a pigment and an adhesive, or a resin layer, or the like) can be coated on an ink recording layer in accordance with the present invention.

[ 0030]

#### Examples

The present invention will be further described by means examples given below.

#### Example 1

Both faces of a paper base having a grammage of  $175\text{g/m}^2$  and a density of  $1.0\text{g/cm}^3$  were provided by corona discharging and the side surfaces of a recording layer were coated (at a melting temperature of  $320^\circ\text{C}$ ) with a polyolefin resin composition 1 used for the surface of the composition and containing titanium dioxide of 10 weight percent mixed and dispersed previously by means of a Bumbury's mixer, using a melt extruder having a T-shaped die so that the coating quantity is  $30\text{g/m}^2$ , at which time a cooling roll provided with mirror finish is used so that said surface coated layer thus cooled has its surface highly smoothened. Also, the opposite face is coated (at a melting temperature of  $320^\circ\text{C}$ ) with a polyolefin composition 1 used for the rear face and having the composition described below by means of the melt extruder having a T-shaped die, so that the coating quantity is  $25\text{g/m}^2$ , said surface being first provided with sandblasting treatment having 120 mesh and then a cooling roll having a surface shape finished with chrome plating being used so that said rear face of the coated layer has its surface



matted, thereby obtaining a sheet-like support.

[ 0031]

Polyolefin Resin Composition 1 for Surface Use

Low density polyethylene resin (Trademark: SHCREX L-182 (phonetic), manufactured by Showa Denko Co., Ltd., density 0.919, melt flow ratio 8g/10 min), 60 weight percent; high density polyethylene resin (Trademark: SHOREX L-191, (phonetic) manufactured by Showa Denko Co., Ltd., density 0.935g/cm<sup>3</sup>, melt flow ratio 11g/10 min), 30 weight percent; anatase type titanium dioxide (manufactured by Ishihara Sangyo, Trademark: A-220), 10 weight percent; stearic acid zinc 0.1 weight percent; antioxidant (manufactured by Ciba Guigy, IRGANOX 1010 (phonetic)) 0.05 weight percent; ultramarine blue (manufactured by Daiichi Kasei, Trademark: AOKUCHI GUNJO No. 2000 (phonetic)) 0.01 weight percent.

[ 0032]

Polyolefin Resin Composition 1 for Rear Face Use

High density polyethylene resin (Trademark: SHOREX L-191 (phonetic), manufactured by Showa Denko Co., Ltd., density  $0.935\text{g/cm}^3$ , 65 weight percent; low density polyethylene resin (Trademark: SHOREX L-170 (phonetic) manufactured by Showa Denko Co., Ltd., density  $0.917\text{g/cm}^3$ , melt flow ratio 7g/10 min) 35 weight percent.

[ 0033]

Next, after providing the surface of the polyethylene resin coated layer on the surface side of the support with corona discharging treatment, as a thermoplastic, hydrophilic resin, a polyvinyl alcohol inducing medium containing an oxyalkylene (manufactured by Kuraray Co., Ltd., Trademark: CP-1000, melt flow ratio (sic) (MFR) 2g/10 min, density  $1.25\text{g/cm}^3$ , melting point  $174^\circ\text{C}$ ) is coated by melt extrusion at a melting point of  $190^\circ\text{C}$ , at a processing speed of 20m/min and in a coating quantity of  $50\text{g/m}^2$  and at the same time cooled using a cleaning roll treated with mirror finish to form a polyvinyl alcohol layer having specular gloss.

[ 0034]

Example 2

After the surface of a polyethylene resin coated paper manufactured in a similar manner to that in Example 1 is treated with corona discharging, as a thermoplastic hydrophilic resin, methylated polyvinyl alcohol consisted of a composition having an acetyl vinyl unit and a vinylalcohol unit having a hydrophilic radical in the side chain (manufactured by Nippon Gohsei Kagaku Kogyo Co., Ltd., Trademark: ECOMATY AX2000, (phonetic) melt flow ratio (sic) (MFR) 20g/10 min, density  $1.27\text{g/cm}^3$ , melting point  $100^\circ\text{C}$ ) is coated by melt extrusion at a melting temperature of  $220^\circ\text{C}$ , at a processing speed of 20m/min and in a coating

quantity of 40g/m<sup>2</sup> and at the same time cooled by a cooling roll provided with mirror finish to form an ink recording layer having specular gloss.

[ 0035]

#### Example 3

After the surface of a paper base having a grammage of 175g/m<sup>2</sup> and a density of 1.0g/cm<sup>3</sup> is treated with corona discharging, as a thermoplastic hydrophilic resin, methylated polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Trademark: CP-2000, melt flow rate (MFR) 2g/10 min, density 1.24g/cm<sup>3</sup>, melting point 130°C) is coated by melt extrusion at a melting temperature of 180°C, at a processing speed of 20m/min and in a coating quantity of 20g/m<sup>2</sup> and at the same time cooled using a cooling roll provided with mirror finish to form an ink recording layer having specular gloss.

[ 0036]

#### Example 4

##### Preparation of Resin Composition

Polyoxyethyleneallylether of 25 moles of additional oxyethylene and acetyl vinyl are copolymerized in methanol under the presence of azo-bis-isobutyronitrile as a catalyst to thereby obtain a copolymer having a polyoxyethylene (meta) allylether unit of 20 weight percent and an acetyl vinyl unit of 80 weight percent. Succesively, saponification is made in a usual manner to obtain a vinylalcohol-based copolymer containing an oxyethylene radical having an acetyl vinyl component saponified to a degree of 93 mol %. This copolymer has a melt flow rate of 15g/10 min, a density of 1.15g/cm<sup>3</sup> and a melting point of 200°C. Succesively, the powdered product of the vinylalcohol-based copolymer containing an oxyethylene radical is dried to reduce the moisture content to below 0.1 weight percent and after an ink recording

composition prepared in the following formula is premixed in a Bumbury's mixer, it is mixed and dispersed by a double-axle extruder to be extruded into the form of a line and is pelletized.

[ 0037]

Formula for Recording Layer

Said vinylalcohol-based polymer containing an oxyethylene radical 100 weight percent; Low density polyethylene (manufactured by Mitsui Sekiyu Kagaku Kogyo Co., Ltd., Trademark: MIRASON-14P (phonetic), density 0.919, melt flow ratio 5.1g/10 min, melting point 107°C) 2 weight percent; Fine silica (mean particle size:  $1.5\mu$  m) 2 weight percent; Corn starch 2 weight percent; Glycerin 5 weight percent.

[ 0038]

Successively, after the surface of a polyethylene resin coated paper manufactured in a similar manner to that in Example 1 is treated with corona discharging, said ink recording layer composite is coated by melt extrusion at a melting temperature of 220°C, at a processing speed of 20m/min and in a coating quantity of 40g/m<sup>2</sup> and at the same time cooled using a cooling roll provided with mirror finish to form an ink recording layer having specular gloss.

[ 0039]

Example 5

After the surface of a paper base having a grammage of 107g/m<sup>2</sup> and a density of 0.75g/m<sup>3</sup> is treated with corona discharging, as a thermoplastic resin, a polymer resin containing polyethylene oxide (manufactured by Daiichi Kogyo Co., Ltd., Trademark: PAOGEN PP-15 (phonetic), melt flow ratio (sic) (MFR) 30g/10 min, density 1.07g/cm<sup>3</sup>, melting point 55°C) is coated by melt extrusion at a melting temperature of 150°C, at a processing temperature (sic) 10m/min and in a coating quantity of

20g/m<sup>2</sup> and at the same time cooled using a cooling roll provided with mirror finish to form an ink recording layer having specular gloss.

[ 0040]

#### Example 6

After the surface of a paper base having a grammage of 104g/m<sup>2</sup> and a density of 0.85g/m<sup>3</sup> is applied with corona discharging, as a thermoplastic resin, an ethylene vinylalcohol resin (manufactured by Kuraray Co., Ltd., Trademark: EVER EP-H105 (phonetic), melt flow ratio (sic) (MFR) 5.5g/10 min, density 1.14g/cm<sup>3</sup>, melting point 165°C) is coated by melt extrusion at a melting temperature of 230°C, at a processing speed of 10m/min and in a coating quantity of 20g/m<sup>2</sup> and at the same time cooled using a cooling roll provided with mirror finish to form an ink recording layer having specular gloss.

[ 0041]

#### Reference 1

A calendered paper for ink jet recording on the market, which contains components, such as a non-absorbent inorganic pigment and a gluing agent, and is provided with an ink recording layer having the surface smoothened (manufactured by Canon Inc., Trademark: GP-101).

[ 0042]

#### Reference 2

After the surface of a polyethylene coated paper manufactured in a similar manner to that in Example 1 is provided with corona discharging, it is coated by a bar coding method with an ink recording layer having composition described below and prepared with a water-based coating, so that the coating quantity is 12g/m<sup>2</sup>.

#### Formula for Ink Recording Layer

Fully saponified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Trademark: KURARAY POBAL 117

(phonetic)) 93 weight percent; Bridging agent (manufactured by Showa Denko Co., Ltd., Trademark: PAPICOL J-003 (phonetic)) 7 weight percent.

[ 0043]

#### Reference 3

After the surface of a polyolefin resin coated paper manufactured in a similar manner to that in Example 1 is provided with corona discharging, it is coated by a bar coating method with hydrophilic resin having thermoplasticity used in Example 1 and after being dissolved in water, so that the coating quantity is 15g/m<sup>2</sup>. In other words, methylated vinylalcohol (manufactured by Nippon Gohsei Kagaku Kogyo Co., Ltd., Trademark: ECOMATY AX2000 (phonetic), melt flow rate (MFR) 20g/10 min, density 1.27g/cm<sup>3</sup>, melting point 199°C) is dissolved to prepare a coating, so that the concentration is 20 weight percent.

[ 0044]

#### Reference 4

After the surface of a paper base having a grammage of 175g/m<sup>2</sup> and a density of 1.0g/cm<sup>2</sup> is applied with corona discharging, it is coated with a low density polyethylene resin (manufactured by Mitsui Sekiyu Kagaku Kogyo Co., Ltd., Trademark: MIRASON M-11P (phonetic), melt flow rate (MFR) 7.2g/10 min, density 0.917g/cm<sup>3</sup>, melting point 106°C) as a thermoplastic resin by melt extrusion at a melting temperature of 260°C, at a processing speed of 20m/min and in a coating quantity of 30g/m<sup>2</sup> and at the same time cooled using a cooling roll provided with mirror finish to thereby obtain a surface having specular gloss.

[ 0045]

#### Evaluation

The gloss and image sharpness of the ink jet recording media of the respective examples and the references, and the gloss, image sharpness and ink

absorbing quality of a solid portion after printed/recorded by an ink jet printer on the market (manufactured by Hulett Packard, Trademark: DESKJET 560J (phonetic)) were evaluated by the procedure as read below.

(1) Glossiness

With respect to a solid portion developed with color inks of yellow, magenta and cyan and a white portion, measurement took place with a glossmeter (manufactured by Nihon Denshoku Kogyo Co., Ltd., Trademark: VG-10) in accordance with the method regulated by JIS-Z-8714 (specular glossiness having an incident angle of  $60^\circ$  and a light receiving angle of  $60^\circ$ ) and the values in the five cycles of measurement were averaged.

[ 0046]

(2) Image Sharpness

With respect to a solid portion developed with color inks of yellow magenta and cyan and a white portion, measurement took place for values in the case of using an optical comb of 2mm wide, out of those for image sharpness stipulated in JIS-K-7105, and the measured values in five cycles were averaged.

[ 0047]

(3) Ink Absorbing Quality

With regard to the ink absorbing quality, measurement took place for the length of time from the time when a woodfree paper was pressed against a printed solid portion to the time when the ink transferred on the woodfree paper disappeared. Evaluation was made in three steps (O: 7 sec or less ,  $\Delta$  : 7-15 sec, X: 15 sec or more). The evaluation result reads below.

[ 0048]

Table 1

	Glossiness	Image Sharpness	Ink
	Solid Portion/ White Portion	Solid Portion/ White Portion	Absorbility
Example 1	75/85	70/75	○
Example 2	70/83	68/72	○
Example 3	69/82	63/67	○
Example 4	75/80	70/75	○
Example 5	70/75	60/65	○
Example 6	58/75	62/60	○
Reference 1	60/65	30/50	
Reference 2	70/75	60/65	X
Reference 3	55/60	30/50	△
Reference 4	- /80	- /75	X

[ 0049]

It has been proved that ink jet recording sheet of Examples 1 - 6 in accordance with the present invention is good in ink absorbing quality and superior in glossiness and image sharpness, while an ink jet recording sheet of Reference 1 out of the scope of the present invention is inferior in glossiness and image sharpness before and after ink recorded. An ink jet recording sheet of Reference 2 had insufficiency in ink absorbing quality. Reference 3 obtained by coating it with a coating layer having composition entirely equal to that of the present invention as water-based coating and drying it, was inferior in glossiness and image sharpness, and was inferior also in ink absorbing quality because the coating quantity could not increase more than 15g/m<sup>2</sup> in the case of water-based coating. Reference 4 was, because its recording layer was formed using multi-purpose thermoplastic resin without having hydrophilic properties, extremely worse in ink



absorbing quality, with the result that no print-recording could not be performed at all.

[ 0050]

Effects of the Invention

An ink jet recording sheet in accordance with present invention is formed by means of a melt extrusion coating method of coating a resin composite containing hydrophilic resin having thermoplasticity as an ink recording layer, thereby obtaining an recording image excellent in ink absorbing quality and having high glossiness and mapping quality and thus providing extreme usefulness in practical use.